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(54) **Method for fabrication of dielectric thin film**

Verfahren zur Herstellung einer elektrischen Dünnschicht

Procédé pour fabriquer une couche mince diélectrique

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- **PATENT ABSTRACTS OF JAPAN vol. 17 no. 683 (E-1477) ,15 December 1993 & JP-A-05 234809 (ISHIHARA KAZUYA) 10 September 1993,**
- **BRIAN CHAPMAN: 'Glow Discharge Proceses', JOHN WILEY AND SONS, INC.**

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Description

II. BACKGROUND OF THE INVENTION

[0001] The present invention relates to electronic functional thin films, and more particularly relates to a method and apparatus for fabricating oxide dielectric thin films.

[0002] In recent years, a dielectric material having a perovskite structure, which has the composition of ABO_3, has been attracting special interest as a thin film material. Here, the site A comprises at least one element from lead (Pb), barium (Ba), strontium (Sr) and lanthanum (La), and the site B comprises at least one element from titanium (Ti) and zirconium(Zr), respectively.

The ferroelectric material represented by $(Pb_{1-x}La_x)(Zr_y Ti_{1-y})_{1-x/4}O_3$ system or $BaTiO_3$ system is excels in ferroelectricity, piezoelectricity, pyroelectricity, electrooptical effect, or the like and a variety of functional devices utilizing the ferroelectric material have been under study. Especially, an application of the ferroelectric material in the new device of "non-volatile memory" has been sought after with great expectations in the area of semiconductor ICs.

Although the material of $SrTiO_3$ system does not show ferroelectricity, the material is expected to be applied in a capacitor insulating film for a super-high density DRAM as a material of high dielectric coefficient.

[0003] For the sake of improvement in characteristics or enhancement in integration extent with these materials, it is very important to make thin films of these materials.

[0004] When it comes to realization of a high performance with these materials, it is desirable to have them processed to take the form of a single crystal film or an orientation film and, in that regard, it is important to develop a hetero-epitaxial growth technology.

The studies on the foregoing have been carried out at many research institutions utilizing various thin film deposition methods, and it can be said that studies on certain particular material systems have already been in completion, provided the discussion is limited to the experimental stage.

However, generally, it has not been easy to produce thin films of required characteristics and good reproducibility by controlling composition, crystalline structure or the like at the stage of a practical and mass-producible process.

[0005] The crystallinity of thin films is basically controlled by substrate materials, chemical compositions, and deposition temperatures.

In general, when lattice mismatching with substrates is minimized and deposition methods of enhanced activation are employed to realize matching in chemical compositions, crystalline thin films will be gained at the crystallization temperature.

According to the sputtering method which has been generally used in making thin films of oxide dielectric Substance, a high substrate temperature of around 600 °C and an oxidizing atmosphere are needed to get crystalline thin films. However, the differences in chemical composition between sintered oxide bodies serving as target materials and deposited thin films are likely to be created, and further, depending on the subtle differences in sputtering conditions, marked adverse effects will be observed in compositions, crystallinity, morphology or the like.

These adverse effects have been constituting a not small obstackle in the mass-production process for thin films wherein uniformity and reproducibility are important. Particularly, although an increased deposition speed desirably contributes to enhancing the through-put in mass-production, the thin films deposited at a high speed under a thermally non-equilibrium condition have tended to cause such problems as excessively small crystal grains, inferior morphology, lack of stability, or the like.

III. SUMMARY OF THE INVENTION

[0006] The object of the present invention is to provide a method and apparatus for mass-producing perovskite type oxide dielectric thin films with high through-put, and good stability, uniformity, and reproducibility.

In order to achieve the foregoing object, the method for producing thin films as disclosed by the present invention is to stabilize deposited thin films in steps for enhancement of the quality of the dielectric thin films by an intermittent introduction of a non-deposition step while the substrate temperature is kept at around the deposition temperature of the perovskite type dielectric thin films at the time of the deposition performed under the condition of a high deposition speed.

Particularly, as the specific means to achieve the foregoing, a plurality of substrates are prepared in advance and said respective substrates are passed over the source of deposition periodically to complete a periodically repeating process of [deposition] - [stabilization] - [deposition] - [stabilization]····, and realize a process which excels in through-put.

In addition, the present invention is to control the concentration of oxygen contained in the thin films and realize thin films of good quality showing an extremely small number of defects at a low substrate temperature in the non-deposition process (i) by causing a decomposition excitation of reactive gases due to plasma to take place on or near the deposition surface in a gaseous atmosphere comprising a gas which reacts with the elements to compose the thin films, or (ii) by causing an oxidation reaction to take place on the deposition surface in a gaseous atmosphere comprising at least ozone (O_3), or (iii) by irradiating light of short wave length on the deposition surface in a gaseous atmosphere comprising at least reactive elements.

[0007] More specifically, the present invention concerns a method for fabrication of dielectric thin films

formed of ABO_3 perovskite type composite compounds, which are composed of the side A comprising at least one element from lead, barium, strontium and lanthanum, the site B comprising at least one element from titanium and zirconium, and oxygen, which is characterized in that it comprises the following steps : deposition process, wherein thin films are deposited on a substrate, and non-deposition process, wherein no deposition of thin films is performed, which are alternatively repeated, while the temperature of said substrate is kept at a specified temperature and in the presence of at least oxygen atoms.

[0008] In one embodiment of the present invention, a sputtering method is used as the thin film deposition process, the substrate is passed over targets periodically, and the deposition process that is performed on the targets and the non-deposition process are periodically repeated.

[0009] In another embodiment of the present invention, the non-deposition process is a process of treating the surface of deposited thin films in an atmosphere comprising activated oxygen species, which react with the raw material elements contained in the thin films, both being excited by plasma.

[0010] In still another embodiment of the present invention, the non-deposition process is a process of treating the surface of deposited thin films in a gaseous atmosphere comprising at least activated oxygen species generated from ozone (O_3) to cause an oxidation reaction thereto.

[0011] In still another embodiment of the present invention, the non-deposition process is a process of irradiating short wave length light on the surface of deposited thin films in a gaseous atmosphere comprising at least activated oxygen species.

[0012] An apparatus for fabrication of the dielectric thin films of the application comprises a substrate holder and a means to keep the temperature of the substrate to be processed to a temperature at which perovskite type crystalline thin films are obtainable, inside a sputtering chamber and possibly also a vacuum chamber, The appararus further comprises : means suitable for driving in rotation said substrate holder supporting at least one substrate to be processed, for making said substrate alternatively undergo a deposition process and a non deposition process, and means for providing oxygen atoms inside said sputtering chamber or said vacuum chamber.

[0013] The apparatus further comprises inside the sputtering chamber, a slitting plate separating said substrate holder and at least one target to be used for the deposition process, a heating light source so as to heat said substrate, and a gas intake providing the inside of said sputtering chamber with a mixed atmosphere of argon and oxygen.

[0014] The apparatus further comprises a partition dividing said vacuum chamber in a deposition chamber in which the thin films formed of ABO3 perovskite type composite compounds are deposited on said substrate, and a non deposition chamber.

[0015] The non deposition chamber can comprise a plasma processing electrode and a plasma supply source so as to provide the substrate with excitation seeds/activation seeds by plasma discharge, an ozone intake for providing the substrate with active oxygen by oxidation processing, and a light source for irradiating short wave length light on said substrate.

[0016] The deposition chamber is provided with a DC or HF power source for the deposition process of said substrate, a first gas intake, which provides a mixed atmosphere of Argon and oxygen into said deposition chamber, and a second gas intake, which provides oxygen (O_2).

IV. BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Fig. 1 is a basic schematic side view of an apparatus for fabricating the thin films of the present invention.

[0018] Fig. 2 shows an X-ray diffraction pattern to represent the crystalline properties of a dielectric thin film of the present invention.

[0019] Fig. 3 is a diagram to show a performance of the deposition process of a dielectric thin film of the present invention.

[0020] Fig. 4 is a basic schematic cross-sectional view of an apparatus for fabricating the thin films of the present invention.

[0021] Fig. 5 is a graph to show the relative dielectric constants of a dielectric thin film of the present invention.

[0022] Fig. 6 is a basic schematic cross-sectional view of an apparatus for fabricating the thin films presented of the present invention.

[0023] Fig. 7 is a graph to show the relative dielectric constants of a dielectric thin film of the present invention.

[0024] Fig. 8 is a basic schematic cross-sectional view of an apparatus for fabricating the thin films of the present invention.

[0025] Fig. 9 is a graph to show the relative dielectric constants of a dielectric thin film of the present invention.

Key to Symbol

[0026]

1	Sputtering Chamber
2	Target
3	Target
4	Target
5	Substrate
6	Substrate Holder
7	Light Source
8	Slitting Plate
9	Vacuum Chamber
10	Exhaust Hole
11	DC or HF Power Source

12 Electrode & Target Holder
13 Electrode & Substrate Holder
14 First Gas Intake
15 Target
16 Substrate
17 Plasma Processing Electrode
18 Plasma Supply Source
19 Support Shaft
20 Second Gas Intake
21 Partition
22 Vacuum Chamber
23 Exhaust Hole
24 DC or HF Power Source
25 Electrode & Target Holder
26 Electrode & Substrate Holder
27 First Gas Intake
28 Target
29 Substrate
30 Ozone Intake
31 Ozone Generating Source
32 Support Shaft
33 Oxygen Gas Intake for Ozone Generating Source
34 Partition
35 Vacuum Chamber
36 Exhaust Hole
37 DC or HF Power Source
38 Electrode & Target Holder
39 Electrode & Substrate Holder
40 First Gas Intake
41 Source of Short Wave Length Light
42 Support Shaft
43 Substrate
44 Second Gas Intake
45 Partition

V. DETAILED DESCRIPTION OF THE INVENTION

[0027] The details of the present invention will be described with the help of its exemplary embodiments.

[0028] Fig. 1 shows how an apparatus for fabricating the dielectric thin films of the present invention is structured. The said apparatus uses a magnetron sputtering system for fabricating perovskite type oxide dielectric thin films. Inside a sputtering chamber 1, there are sputter targets 2, 3, and 4 formed of
a sintered oxide ferroelectric material and disposed on one circumference at positions symmetrical with one another to make it possible to perform a simultaneous sputtering deposition with upto three elements at the maximum.

A substrate 5 is disposed on a substrate holder 6 in a radial direction so as to pass immediately over the targets 2, 3, and 4 when the substrate holder 6 is rotated.

A lamp heating system by a light source 7 is used as the method for heating the substrate.

According to the foregoing set-up, each respective target is sputtered in a mixed atmosphere of argon (Ar) and oxygen (O_2) while the substrate holder is rotated, resulting in a periodical change of the deposition speed of thin films according to the positional relations between the substrate and targets under the condition of a specified substrate temperature.

The time of said periodic change can be altered by the rotational speed of the substrate holder 6 and the number of the targets used.

The maximum deposition speed of thin films can be adjusted to the most suitalbe value by controlling the sputtering conditions such as sputtering electric power and the like. Besides, a slitting plate 8 has holes of suitable shapes to ensure a realization of the fundamental properties of thin films such as uniformity in composition, and the like.

The substrate holder 6 is floated in terms of electric potential to suppress the impacts inflicted by electrons and ions from plasma.

[0029] Next, the case wherein $Pb_{0.9}La_{0.1}Ti_{0.975}O_3$ films are formed will be explained as one of the exemplary embodiments of the present invention.

A sintered ferroelectric material [$Pb_{0.9}La_{0.1}TiO_3$ + 0.2PbO] (6 inches in diameter) was used as the targets 2, 3, and 4, and the (100) plane of magnesium oxide (MgO) was used as the substrate 5 to form a thin film of 2 to 3 µm thick.

[0030] It was confirmed that the substrate temperature ranging from 550 to 650 °C is suitable to form a high crystallinity thin film of perovskite structure.

It was also confirmed that Ar/O_2 - = 20 to 5 is suitalbe as the mixing ratio of Ar to O_2, and 0.1 to 0.5 Pa is suitalbe as the pressure.

Also, a deposition speed of 0.5 to 2.5 Å/s was achieved with the target to substrate distance set at 80 to 90 mm and the input power set at 200 to 400 W per one target.

[0031] Crystal properties, morphology, and the like of thin films were changed according to said sputtering conditions, and also such electrical characteristics as dielectric constant, pyroelectric constant, or the like are changed.

These changing aspects are dependent on material compositions and it is needed to optimize the material compositions on a case by case basis.

[0032] By setting forth the foregoing sputtering conditions, the deposition speed of the thin films located immediately above each respective target will be decided, but changes by time of the deposition speed and an average forming speed of the thin films will be dependent on the number of targets used and the rotational speed of the substrate holder.

[0033] First, a deposition speed and properties of the thin films formed were investigated with a substrate disposed immediately above a target while the substrate holder being kept in a non-rotating state.

In this case, the average forming speed was, as a matter of course, the same as the deposition speed.

The deposition speed was controlled mainly by the input power to the target and could be changed upto 2.5 Å/s at maximum, at which the target was kept intact and in

a stabilized condition.

[0034] According to the analysis result of a plasma emission spectrochemical method, the metallic element composition ratio of the formed thin films was confirmed to be almost in agreement with the stoichiometrical ratio of Pb : La : Ti = 0.9 0.1 : 0.975 except for the composition ratio of Pb which deviates by about 10 %.

According to the analysis result of an X-ray diffraction method, the crystal properties of the thin films, as shown in Fig. 2, indicated an existence of the perovskite structure and also the lattice constants a = 3.94 Å, b = 4.09 Å as estimated from the diffraction peaks (001), (100), (002) and (200) were confirmed to be in a good agreement with the values mentioned in literature.

Also, the diffraction peaks (001) and (002) are remarkably strong and it is known that the orientation is strong in the direction of the c-axis serving as the polarization axis.

In electrical characteristics, the thin films having excellent crystallinity and a high c-axis orientation show a large pyroelectric constant and an appropriately small dielectric constant ε which make it possible to anticipate a high sensitivity (proportionate to γ/ε) when used in infrared sensors, and further, excellent characteristics when used in non-volatile memory devices.

There are a full width at half maximum (FWHM) of the diffraction peak (001) and a c-axis orientation ratio $\alpha = I(001) / [I(001) + I(100)]$ as the indexes relative to the crystal properties that can be read from the X-ray diffraction data.

(Note: I(001) and I(100) are the diffraction strength at the peaks (001) and (100), respectively.)

When an evaluation was conducted with thin films prepared under a deposition speed ranging from 0.5 to 2.5 Å/s, FWHM = 0.2° and = 96 to 100 % were obtained. As far as a judgment is made from these data, it is considered that thin films of excellent crystallinity were produced irrespective of the deposition speed.

[0035] Next, the thin films were isolated through etching the MgO substrate, disposed with electrodes on each respective surface of the front and back thereof, and the electrical properties across the film thickness, mainly pyroelectric characteristics, were evaluated.

The results of the evaluation of the dielectric constant ε and pyroelectric constant γ showed that there was an upper limit in the deposition speed at which thin films with

a sensor sensitivity as high as $\varepsilon \sim 170$ and $\gamma \sim 5 \times 10^{-8}$ C/cm^2·K could be produced, and the limit was 1.8 Å/s. The thin films formed at a deposition speed higher than 1.8 Å/s tended to show a low sensor sensitivity of $\varepsilon \sim 400$ and $\gamma \sim 4 \times 10^{-8}$ C/cm^2·K at 2.5 Å/s, for example.

The foregoing is considered to be involving a problem attributable to morphology or stability of the growth condition of the crystal grains or the like.

The upper limit in the deposition speed as observed above was varied according to the composition of the compounded thin films and the film formation condition thereof, and was confirmed by the inventors to fall within the range of 1.0 to 2.0 Å/s.

[0036] The inventors examined an intermittent and periodical introduction of a stabilizing process of non-deposition,

wherein no thin films are deposited, for assuring a sufficient growth and stabilization of crystal grains even under the condition of a high deposition speed.

When the targets 2 and 3 only are sputtered and the substrate holder 6 is rotated in Fig. 1, a deposition process and a non-deposition process of nearly ~0 Å/s deposition speed will be alternatingly taking place, as shown in Fig. 3, and the average formation speed will be about 1/3 of the speed of the deposition taking place on the targets. While keeping the deposition speed on the targets at 2.5 Å/s, which produced previously only a low sensor sensitivity with said substrate holder kept in a non-rotating condition, the substrate holder was rotated at 4 rpm, and the effect of introducing a non-deposition process periodically.was investigated.

In this case, the formation time was extended three times before gaining the same film thickness.

The result of an X-ray diffraction measurement of the formed thin film showed good crystallinity of FWHM = 0.2° and α = 98 %, and also pyroelectric characteristics of $\varepsilon \sim 170$ and $\gamma \sim 5 \times 10^{-8}$ C/cm^2·K, which made it possible to anticipate a sensor sensitivity equal to that of the case wherein the deposition speed was low (not higher than 1.8 Å/s in the present exemplary embodiment).

[0037] The foregoing result was considered due to an introduction of the processes to assure a sufficient growth and stabilization of crystal grains that have taken place by steps against the thin films deposited at a high speed, through periodically repeating the processes of [deposition]-[non-deposition (stabilization)) - [deposition] - [non-deposition (stabilization)] ····.

The thin films formed according to the present invention are sufficiently stabilized and considered to excel in long period stability and also in reliability.

[0038] Besides, by having a plurality of substrates prepared and passed over the targets in succession and periodically, much higher through-put will be realized when compared with the case wherein a deposition process is repeated with one target, since the time required in installing the substrate, raising and lowering the temperature, or the like can be greatly reduced.

Even when one large target is used for deposition on all the substrates simultaneously, the places where the substrates are mounted and yet the uniformity in deposition is maintained will be rather scarce.

In this respect, too, the method disclosed by the present invention is superior when it comes to mass-producibility.

[0039] An attempt to enhance the quality of thin films through employing a non-deposition process intermittently has been made on an experimental base, but it was mostly relying on controlling a shutter or a deposi-

tion source, with resultant poor through-put and also concern over a disturbance in the deposition source.

[0040] In the foregoing exemplary embodiment, a non-deposition process, wherein the deposition speed is 0 Å/s was referred to as a stabilizing process. However, in principle, as long as the non-deposition process is a low deposition process (not higher than 1.8 Å/s in the foregoing exemplary embodiment), there will be no problem to deposit over the thin films formed during the period of high speed deposition while said thin films being stabilized.

Further, when the period for continuous formation at a high deposition speed is excessively long, the stabilizing process following thereafter may not sometimes be effective enough. Therefore, it will be further necessary to study the periodic time of periodically changing the deposition speed and the proportion of the high speed deposition period.

[0041] Next, in reference to the foregoing non-deposition process, various methods of realizing thin films of good quality, which have a very small number of defects, by controlling the oxygen content in the thin films will be explained. With regard to (i) a processing method wherein a decomposition excitation of a reactive gas due to plasma takes place on or near the deposition surface in a gaseous atmosphere comprising a gas that reacts with the elements composing the thin films, (ii) a processing method wherein an oxidation reaction takes place on the deposition surface in

a gaseous atmosphere comprising at least ozone (O_3), and (iii) a processing method wherein light of short wave length is irradiated on the deposition surface in a gaseous atmosphere comprising at least reactive elements, one each example thereof will be described hereunder.

[0042] (i) Fig. 4 is a schematic illustration of a sputtering apparatus whereby plasma processing of the devices to be used in the present invention can be performed.

[0043] In Fig. 4, each respective numerical symbol means as follows:

9 Vacuum Chamber
10 Exhaust Hole
11 DC or HF Power Source
12 Electrode & Target Holder
13 Electrode & Substrate Holder
14 First Gas Intake
15 Target
16 Substrate
17 Plasma Processing Electrode
18 Plasma Supply Source
19 Support Shaft
20 Second Gas Intake
21 Partition

[0044] The said apparatus is basically the same as the apparatus of Fig. 1 except for having replaced one of the targets with an electrode 17 for providing the substrate with excitation seeds·activation seeds by plasma discharge decomposition.

A plasma processing power supply source 18 generates plasma by supplying an electric field. Item 20 is a second gas intake for that purpose.

Take the case of forming an oxide thin film, for example. A reactive gas for oxidation such as O_2 or the like only is introduced near the substrate.

In said plasma processing step of non-deposition, numerous activated oxygen elements are generated due to plasma decomposition of gaseous oxygen molecules existing near the substrate and oxidize the defects where oxidation was insufficient or eliminate excessive oxygen from the thin film surface.

As a result, relatively fine and good quality thin films can be formed by deposition without hurting the substrate.

With the apparatus used in the present example, a partition 21 is disposed between the deposition area where targets are placed and the plasma processing area for non-deposition to provide a mixed gas atmuspher of Ar serving as the sputtering gas for the deposition prucess and an O_2 gas atmospher, which is reactive, for the plasma processing step of non-deposition.

[0045] Next, specific aspects of the example will be explained. Fig. 5 shows changes in the relative dielectric constant of lead titanate ($PbTiO_3$) thin films formed under the conditions wherein the substrate temperature was kept constant at 550 C, a high frequency power source (13.56 MHz) was used as the plasma processing power supply source, the electric power density thereof was changed from 0 to 0.1 W/cm^2, and the substrate holder was rotated at 3 rpm.

According to the present example, one 6 inch target for deposition was used, the electrode for plasma disposition was 10 inches in diameter, the time required of the substrate to pass once over the target was about 5 seconds, and the plasma processing was applied for about 6 seconds after deposition of about 1.5 nm.

As clearly observed in Fig. 5, a distinctive improvement in the relative dielectric constant has been realized on account of the excitation reactive seeds provided by plasma. Even when the film deposition was performed under a low substrate temperature, an improvement in the dielectric characteristics was clearly observed.

[0046] (ii) Fig. 6 is a schematic illustration of a sputtering apparatus whereby ozone processing of the devices to be used in the present invention can be performed.

[0047] In Fig. 6, each respective numerical symbol means as follows:

22 Vacuum Chamber
23 Exhaust Hole
24 DC or HF Power Source
25 Electrode & Target Holder
26 Electrode & Substrate Holder
27 First Gas Intake
28 Target
29 Substrate

30 Ozone Intake
31 Ozone Generating Source
32 Support Shaft
33 Oxygen Gas Intake for Ozone Generation
34 Partition

[0048] The said apparatus is basically the same as the apparatus of Fig. 1 except for having replaced one of the targets with an ozone intake 30 for providing the substrate with active oxygen by ozone oxidation processing. Oxygen gas is fed to an ozone generating source 31, and ozone is produced by a silent discharging method, for example, or the like. According to said ozone processing step of non-deposition, numerous active oxygen atoms are generated near the substrate due to plasma decomposition of oxygen gas molecules or the like, for oxidation of the defects where oxidation has been insufficient and also for elimination of the excessive oxygen from the film surface.
As a result, relatively fine and good quality thin films can be formed by deposition without hurting the substrate.

[0049] Next, specific aspects of the example will be presented. Fig. 7 shows changes in the relative dielectric constant of lead titanate ($PbTiO_3$) thin films formed by deposition as the substrate temperature was changed under one condition, wherein the substrate holder was rotated at 3 rpm, and ozone was introduced, and under another condition wherein the substrate holder was rotated at 3 rpm, and no ozone was introduced. The introduced ozone had the form of a mixed gas of the 5 to 10 % ozone produced by silent discharging of oxygen gas and the oxygen gas before reaction.

[0050] According to the present example, one 6 inch target for deposition was used, the electrode for plasma disposition was 10 inches in diameter, the time required of the substrate to pass once over the target was about 5 seconds, and the plasma processing was applied for about 6 seconds after deposition of about 1.5 nm.
As clearly observed in Fig. 7, a distinctive improvement in the relative dielectric constant was realized on account of the process wherein oxidation and crystal growth were able to be promoted by introduction of ozone.
Thus, even when the film deposition was performed under a low substrate temperature, an improvement in the dielectric characteristics was clearly observed.

[0051] (iii) Fig. 8 is a schematic illustration of a sputtering apparatus whereby light irradiation processing of the devices to be used in the present invention can be performed.

[0052] In Fig. 8, each respective numerical symbol means as follows:

35 Vacuum Chamber
36 Exhaust Hole
37 DC or HF Power Source
38 Electrode & Target Holder
39 Electrode & Substrate Holder
40 First Gas Intake
41 Short Wave Length Light Source
42 Support Shaft
43 Substrate
44 Second Gas Intake
45 Partition

[0053] The said apparatus is basically the same as the apparatus of Fig. 1 except for having replaced one of the targets with a light source 41 for irradiating short wave length light on the substrate.
According to said light irradiation step of non-deposition, numerous active oxygen atoms are generated by photolysis of oxygen gas molecules or the like existing near the substrate, for oxidation of the defects where oxidation was insufficient, elimination of the excessive oxygen from the film surface, and also relieving thermally the lattice strain produced in the thin films.
As a result, relatively fine and good quality thin films can be formed by deposition without hurting the substrate.

[0054] Next, specific aspects of the example will be explained. Fig. 9 shows changes in the relative dielectric constant of lead titanate ($PbTiO_3$) thin films formed by deposition as the substrate temperature was changed under the conditions wherein a low pressure mercury lamp was used as the light source with its irradiation amount kept at 0.5 W/cm^2 and the substrate holder was rotated at 3 rpm. According to the present example, one 6 inch target for deposition was used, the electrode for plasma disposition was 10 inches in diameter, the time required of the substrate to pass once over the target was about 5 seconds, and the light was irradiated for about 6 seconds after deposition of about 1.5 nm.
As clearly observed in Fig. 9, a distinctive improvement in the relative dielectric constant was realized on account of the process wherein oxidation and crystal growth were able to be promoted by light irradiation.
Thus, even when the film deposition was performed under a low substrate temperature, an improvement in the dielectric characteristics was clearly observed.

[0055] As explained in the foregoing, thin films of good quality can be obtained by application of plasma processing, ozone processing or light irradiation in the non-deposition process.

[0056] The apparatus for fabrication of the thin films of the present invention can be effectively used in producing thin films of not only the perovskite type oxide dielectric substance but also multi-element oxides, which are similar to high temperature super conductive substances or the like.

[0057] In order to have these materials for thin films actually used, it is necessary to establish mass-producibility, stability, uniformity, and reproducibility thereof. In that regard, the present fabrication apparatus, whereby an excellent process to satisfy both the stability and mass-producibility is realized through having a plurality of substrates passed over a deposition source periodically and through the steps of [high speed deposi-

tion] - [stabilization] - [high speed deposition] - [stabilization] ···· repeated alternatingly, is extremely effective.

[0058] Thus, according to the present invention, a process for fabricating thin films of oxide dielectric substances has been made available for the extremely great benefit of the industry.

The dielectric substances to be used are multi-element oxides, characteristics of which can be greatly influenced not only by the chemical composition and crystallinity but also by the morphology thereof. However, the present invention can certainly contribute to realization of very high precision thin films using these dielectric substances.

Claims

1. A method for fabrication of dielectric thin films formed of ABO_3 perovskite type composite compounds, which are composed of the side A comprising at least one element from lead, barium, strontium and lanthanum, the site B comprising at least one element from titanium and zirconium, and oxygen, **characterized in that** it comprises the following steps :

   deposition process, wherein thin films are deposited on a substrate (5 ; 16 ; 29 ;43) , and non-deposition process, wherein no deposition of thin films is performed,
   which are alternatingly repeated, while the temperature of said substrate (5;16;29;43) is kept at a specified temperature and in the presence of at least oxygen atoms.

2. The method for fabrication of dielectric thin films according to claim 1, wherein a sputtering method is used as the thin film deposition process, the substrate (5;16;29;43) is passed over targets (2,3,4;15;28) periodically, and the deposition process that is performed on the targets (2,3,4;15;28) and the non-deposition process are periodically repeated.

3. The method for fabrication of dielectric thin films according to claims 1 or 2, wherein the non-deposition process is a process of treating the surface of deposited thin films in an atmosphere comprising activated oxygen species, which react with the raw material elements contained in the thin films, both being excited by plasma.

4. The method for fabrication of dielectric thin films according to claim 1 or 2, wherein the non-deposition process is a process of treating the surface of deposited thin films in a gaseous atmosphere comprising at least activated oxygen species generated from ozone (O_3) to cause an oxidation reaction thereto.

5. The method for fabrication of dielectric thin films according to claim 1 or 2, wherein the non-deposition process is a process of irradiating short wave length light on the surface of deposited thin films in a gaseous atmosphere comprising at least activated oxygen species.

Patentansprüche

1. Verfahren zur Herstellung von aus ABO_3-Perovskit-Verbindungen ausgebildeten dielektrischen Dünnschichten, die aus A, das mindestens ein Element aus der aus Blei, Barium, Strontium und Lanthan bestehenden Gruppe aufweist, B, das mindestens ein Element aus der aus Titan und Zirconium bestehenden Gruppe aufweist, und Sauerstoff bestehen, **dadurch gekennzeichnet, dass** es die Schritte

   Auftragen, in dem Dünnschichten auf ein Substrat (5, 16, 29, 43) aufgetragen werden, und Nichtauftragen, in dem keine Auftragung von Dünnschichten erfolgt, umfasst,
   die zumindest in Gegenwart von Sauerstoff-Atomen abwechselnd wiederholt werden, wobei die Temperatur des Substrats (5, 16, 29, 43) auf einer festgelegten Temperatur gehalten wird.

2. Verfahren zur Herstellung dielektrischer Dünnschichten nach Anspruch 1, **dadurch gekennzeichnet, dass** ein Zerstäubungsverfahren als Dünnschichtauftragungsverfahren verwendet wird, dass das Substrat (5, 16, 29, 43) periodisch über Targets (2, 3, 4, 15, 28) geführt wird, und dass das Auftragen auf die Targets (2, 3, 4, 15, 28) und das Nichtauftragen periodisch wiederholt werden.

3. Verfahren zur Herstellung dielektrischer Dünnschichten nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Nichtauftragung ein Prozess der Behandlung der Oberfläche der aufgetragenen Dünnschichten in einer Atmosphäre ist, die aktivierte Sauerstoff-Arten aufweist, die mit den in den Dünnschichten enthaltenen Ausgangsmaterial-Elementen reagieren, wobei beide vom Plasma angeregt werden.

4. Verfahren zur Herstellung dielektrischer Dünnschichten nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Nichtauftragung ein Prozess der Behandlung der Oberfläche der aufgetragenen Dünnschichten in einer Gas-Atmosphäre ist, die mindestens aktivierte Sauerstoff-Arten, die aus Ozon (O_3) erzeugt werden, aufweist, um sie einer Oxidationsreaktion zu unterziehen.

5. Verfahren zur Herstellung dielektrischer Dünn-

schichten nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** die Nichtauftragung ein Prozess der Bestrahlung der Oberfläche der aufgetragenen Dünnschichten mit Licht kurzer Wellenlänge in einer Gas-Atmosphäre ist, die mindestens aktivierte Sauerstoff-Arten aufweist.

Revendications

1. Procédé de fabrication de films minces diélectriques formés de composés composites du type perovskite ABO_3, qui sont composés du site A comprenant au moins un élément parmi le plomb, le baryum, le strontium et le lanthane, le site B comprenant au moins un élément parmi le titane et le zirconium, et de l'oxygène, **caractérisé en ce qu'il** comprend les étapes suivantes :

   un procédé de dépôt, dans lequel des films minces sont déposés sur un substrat (5 ; 16 ; 29 ; 43), et
   un procédé de non-dépôt, dans lequel aucun dépôt de film mince n'est exécuté,
   lesquels sont répétés en alternance, tandis que la température dudit substrat (5 ; 16 ; 29 ; 43) est maintenue à une température spécifiée et en présence d'au moins des atomes d'oxygène.

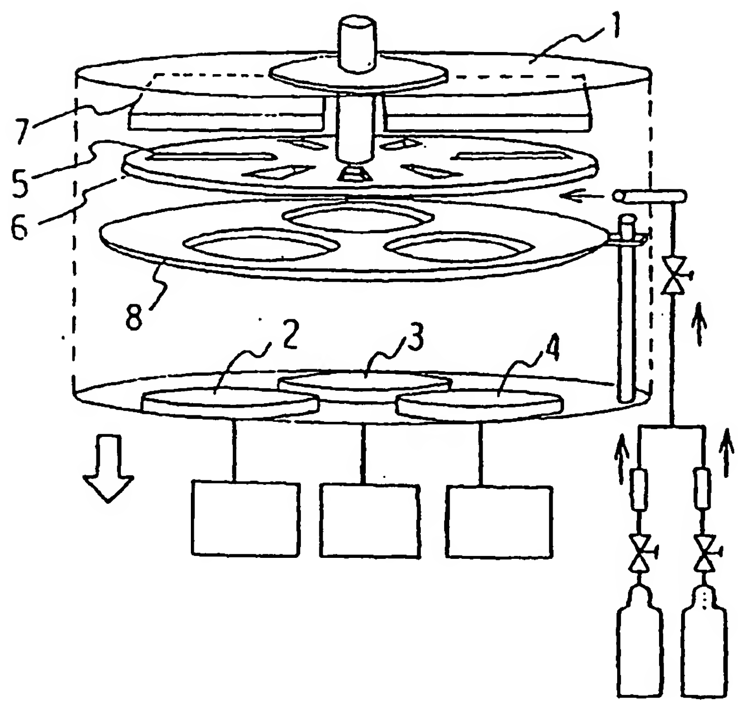
2. Procédé de fabrication de films minces diélectriques selon la revendication 1, dans lequel un procédé de pulvérisation est utilisé en tant que procédé de dépôt de film mince, le substrat (5 ; 16 ; 29 ; 43) passe sur des cibles (2, 3, 4 ; 15 ; 28) de façon périodique, et le procédé de dépôt qui est exécuté sur les cibles (2, 3, 4 ; 15 ; 28) et le procédé de non-dépôt sont répétés de façon périodique.

3. Procédé de fabrication de films minces diélectriques selon la revendication 1 ou 2, dans lequel le procédé de non-dépôt est un procédé de traitement de la surface des films minces déposés dans une atmosphère comprenant des espèces oxygène activées, qui réagissent avec les éléments de matériaux bruts contenus dans les films minces, les deux étant excités par plasma.

4. Procédé de fabrication de films minces diélectriques selon la revendication 1 ou 2, dans lequel le procédé de non-dépôt est un procédé de traitement de la surface des films minces déposés dans une atmosphère gazeuse comprenant au moins des espèces oxygène activées générées à partir d'ozone (O_3) afin de provoquer une réaction d'oxydation sur celle-ci.

5. Procédé de fabrication de films minces diélectriques selon la revendication 1 ou 2, dans lequel le procédé de non-dépôt est un procédé de rayonnement d'une lumière à courte longueur d'onde sur la surface des films minces déposés dans une atmosphère gazeuse comprenant au moins des espèces oxygène activées.

Fig. 1



F i g. 2

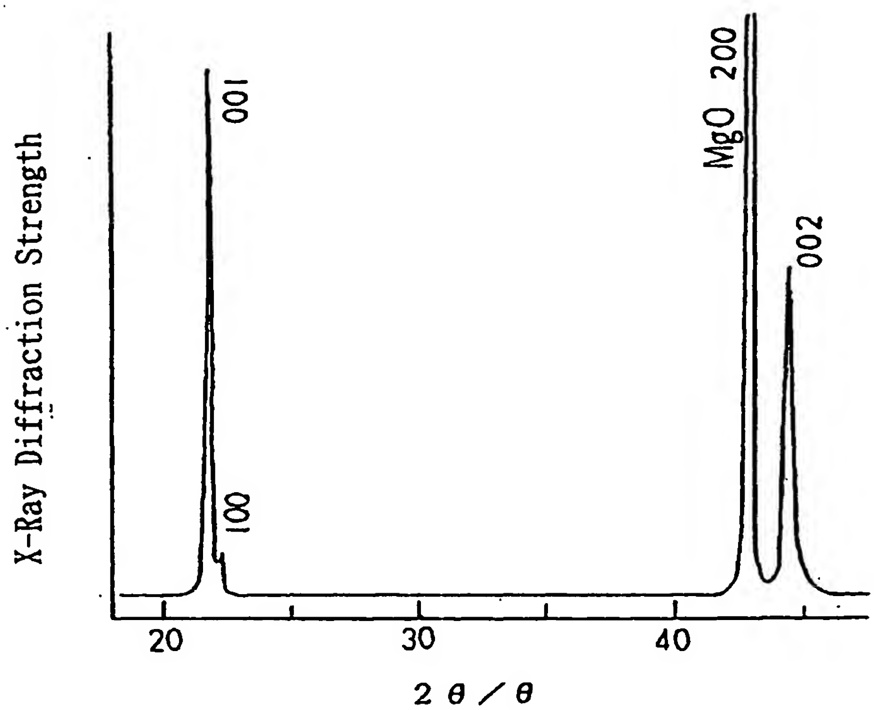


Fig. 3

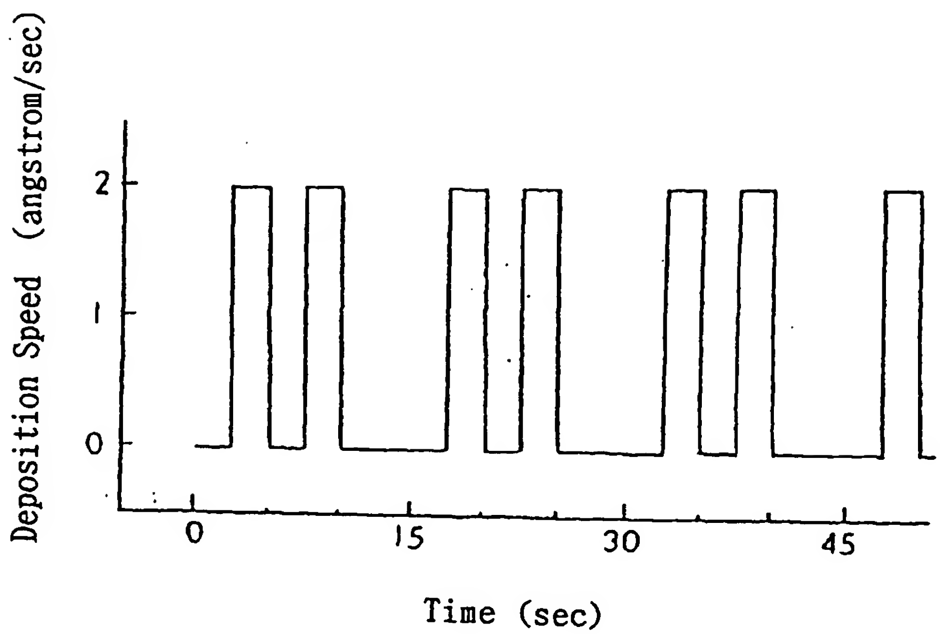


Fig. 4

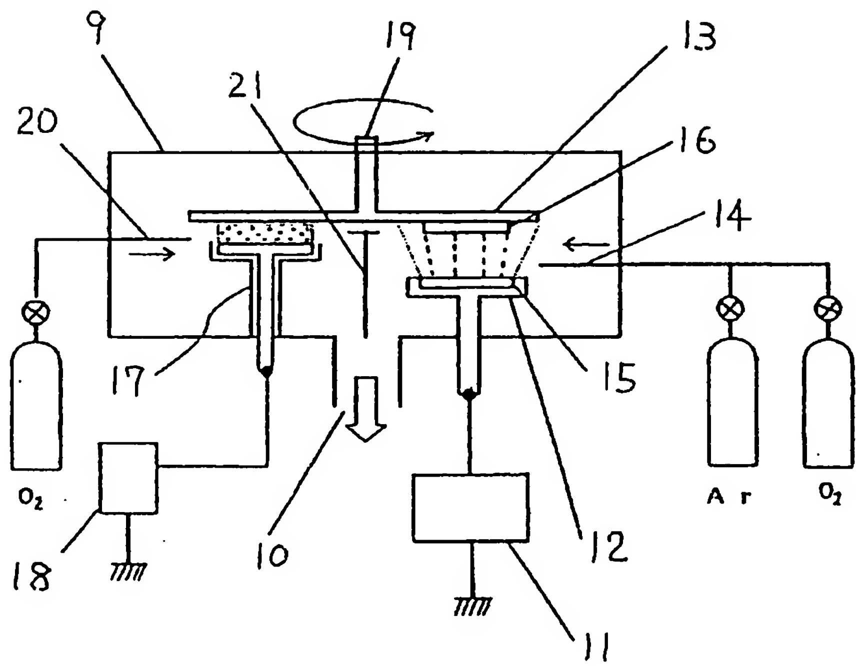


Fig. 5

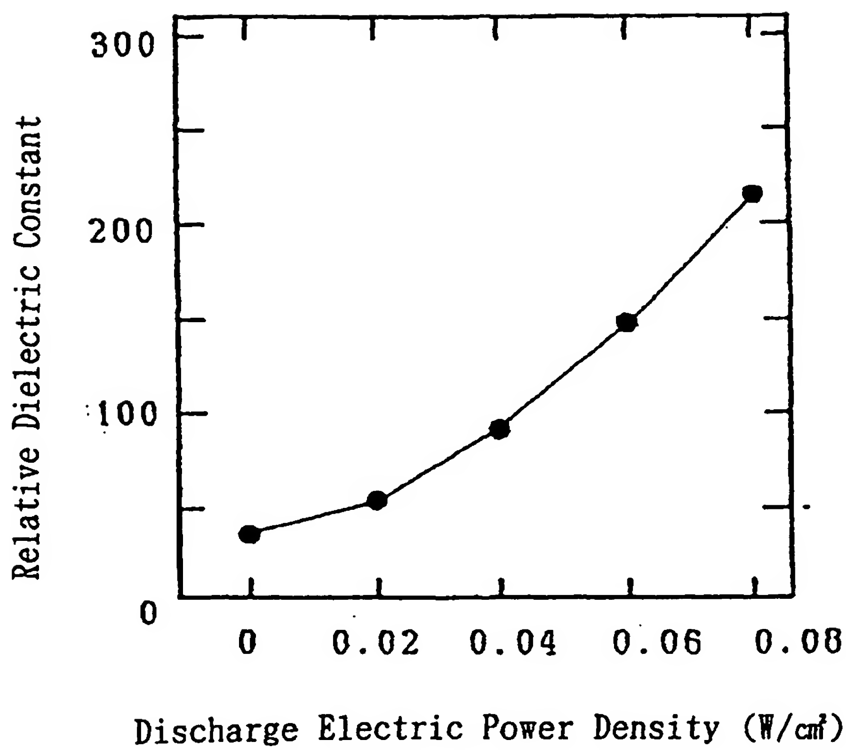

300
200
100
0
Relative Dielectric Constant
0
0.02
0.04
0.06
0.08
Discharge Electric Power Density (W/cm²)

Fig. 6

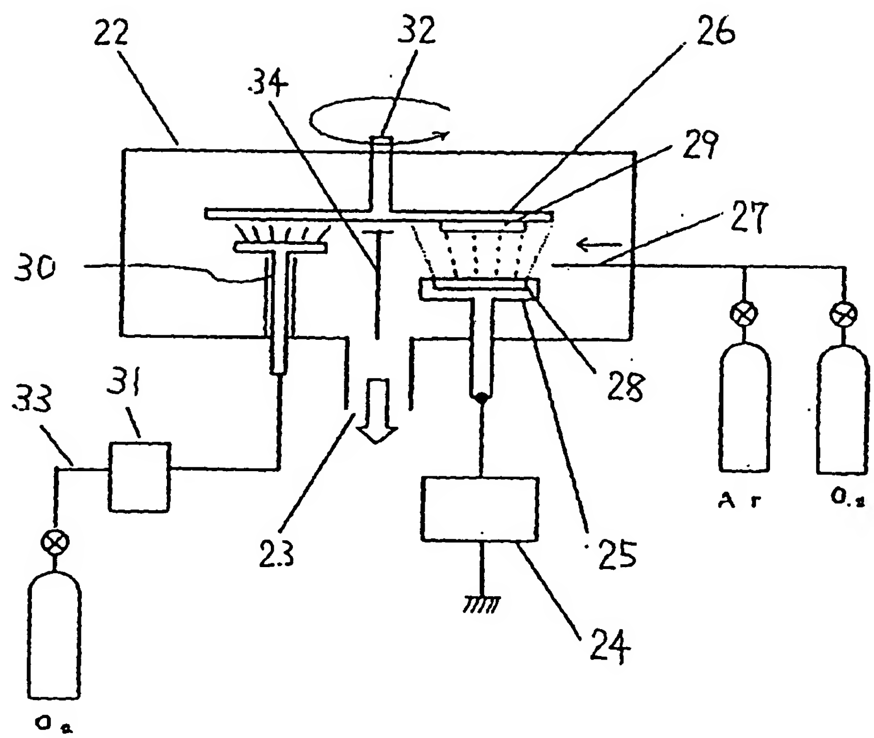
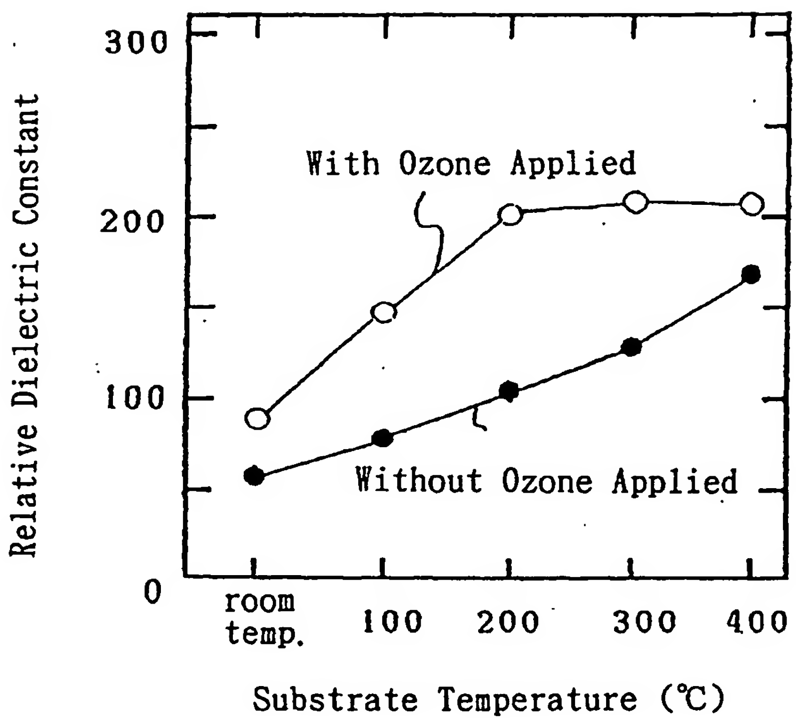


Fig. 7


300
200
100
0
Relative Dielectric Constant
With Ozone Applied
Without Ozone Applied
room temp.
100
200
300
400
Substrate Temperature (℃)

F i g. 8

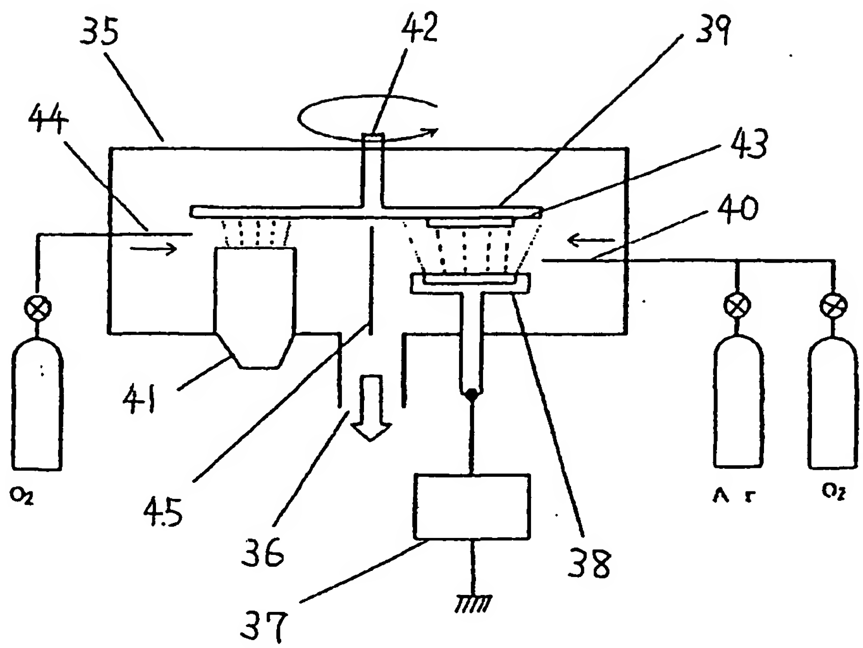
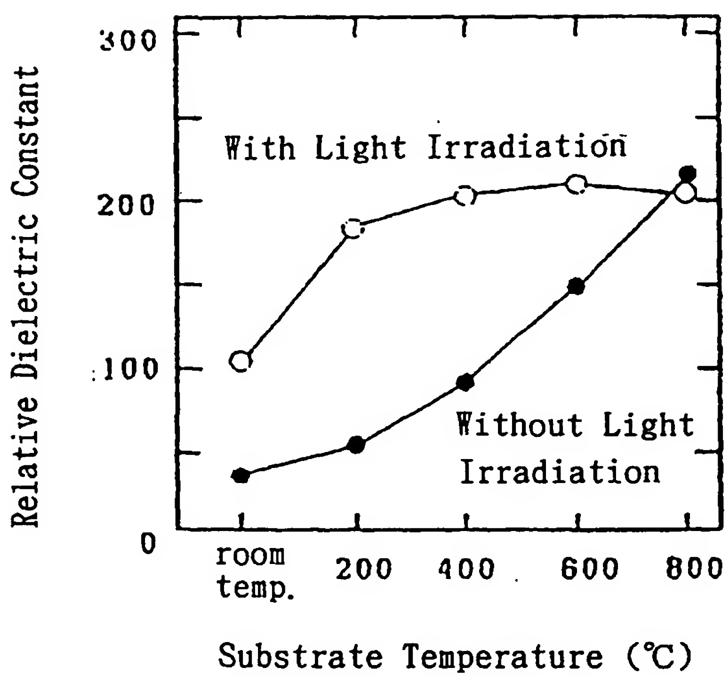


Fig. 9


300
200
100
0
Relative Dielectric Constant
With Light Irradiation
Without Light Irradiation
room temp.
200
400
600
800
Substrate Temperature (℃)